DEVELOPMENT OF SILICA-BASED AND ACTIVATED CARBON-BASED CATALYSTS FOR GLYCEROL ACETYLATION, TRANSESTERIFICATION AND ACETALIZATION PROCESSES FOR THE PRODUCTION OF OXYGENATED FUEL ADDITIVES

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by

MUATAZ SHAKIR KHAYOON

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DEDICATION

This work is dedicated to the spirit of my father, for being my biggest fan and my inspiration, and to my mother, for being my rock and my best friend.

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LIST OF SYMBOLS

Symbol	Description	Unit
A	Pre-exponential factor	L mol^{-1} min^{-1}
a_m	External surface area of the catalyst	
C_{Go}	Initial glycerol concentration	mmol/L
C_G	Glycerol concentration at any time, t	mmol/L
D_e	Diffusivity	
E_a	Activation energy	J/mol
H	Hysteresis loop	
k	Reaction rate constant	min^{-1}
k_m	Mass transfer coefficient	
K_A	Adsorption equilibrium constant	L/mg
K_e	Equilibrium constant	min^{-1}
OH^-	Hydroxyl ion	
P	Pressure	Pa
P_o	Initial pressure	Pa
r_{Go}	Initial rate of reaction	mol/(L.min)
r_s	Surface reaction rate	mol/(L.min)
R^2	Correlation coefficient	
R	Universal gas constant	J/mol.k
X_G	Fractional conversion of glycerol	
X_{Ge}	Fractional conversion of glycerol at equilibrium	
θ_{Ads}	Adsorption coefficient	
θ_m	Magic angle of NMR spinning	Degree
η	Effectiveness factor	
φ_s	Thiele modulus	
ΔG	Gibbs free energy	(J/mol)
ΔH_f	Enthalpy of formation	(J/mol)

LIST OF ABBREVIATIONS

AC	Activated carbon
ASTM	American standards for testing and materials
BET	Brunauer-Emmet-Teller
BJH	Barret-Joyner-Halenda
Ca	Calcium
CO_2	Carbon dioxide
DAG	Diacetyl glycerol
EDX	Energy dispersive X-ray
EN	European standard
FTIR	Fourier transform infrared
GC	Gas chromatography
GC	Glycerol carbonate
HCl	Hydrochloric acid
HPA	Heteropoly acid
H_2O	Water
MAG	Monoacetyl glycerol
Mg	Magnesium
Ni	Nickel
NO_x	Nitrogen oxides
ON	Octane number
SAXS	Samll angle X-ray scattering
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
wt.%	Weight percent
X_{gly}	glycerol conversion
XRD	X-ray diffraction
Y	Yttrium
Zr	Zirconium

PEMBANGUNAN MANGKIN BERASASKAN SILIKA DAN KARBON UNTUK PROSES PENGASETILAN, TRANSESTERIFIKASI DAN PENGASETALAN GLISEROL BAGI MENGHASILKAN BAHAN TAMBAH BAHAN API BEROKSIGEN

ABSTRAK

Pertumbuhan pesat industri biodiesel di seluruh dunia telah membawa kepada penghasilan banyak gliserol yang boleh mempengaruhi ekonomi keseluruhan industri tersebut. Jadi, penyelidikan ke arah peningkatan nilai gliserol menerusi penukarannya kepada aditif bahan api beroksigen adalah amat diperlukan. Gliserol telah ditukarkan secara berasingan kepada gliserol asetat, gliserol asetal dan gliserol karbonat menerusi empat proses bermangkin berbeza iaitu pengasetilan dengan asid asetik, transesterifikasi dengan metil asetat, pengasetalan dengan aseton dan transesterifikasi dengan dimetil karbonat. Mangkin heterogen berbeza iaitu mangkin karbon teraktif tersulfat, SBA-15 hibrid yang terfungsi dengan β-MoO_3 dan SBA-3 berfungsikan yttrium telah dibangunkan untuk penghasilan bahan-bahan hasil yang tersebut di atas. Mangkin-mangkin tersebut telah dicirikan untuk mengkaji sifat-sifat tekstur, jenis kumpulan berfungsi dan morfologi permukaan menggunakan kaedah analisis permukaan, FTIR, XRD, SAXS, ^{31}P MAS NMR, keasidan dan kebesan permukaan, CHNS/O, EDX, SEM dan TEM. Mono-, di- dan triasetil gliserol (MAG, DAG dan TAG, masing-masing) merupakan produk-produk bagi kedua-dua tindakbalas pengasetilan dan transesterifikasi dengan metal asetat. Gelang asetal lima dan enam ahli merupakan produk tindakbalas bagi proses pengasetalan manakala gliserol karbonat merupakan bahan bernilai tinggi yang diperolehi menerusi proses transesterifikasi dengan dimetil karbonat. Bagi tujuan meningkatkan lagi penghasilan DAG dan TAG, tindakbalas transesterifikasi gliserol dengan metil asetat kemudiannya diselidiki menggunakan mangkin SBA-3 berfungsikan yttrium.

3%Y/SBA-3 dengan luas permukaan yang tinggi (1568 m^2 g^{-1}) merupakan mangkin yang paling aktif untuk proses pengasetilan gliserol. Penukaran lengkap gliserol dicapai oleh mangkin ini dengan kememilihan terhadap MAG, DAG, dan TAG adalah masing-masing 10%, 35% and 55%. Mangkin yang sama juga begitu aktif dalam proses pengesteran gliserol dengan metal asetat yang membawa kepada penukaran gliserol yang lengkap pada nisbah mol gliserol/metil 1:12 dan 110 ^oC dengan kememilihan bagi MAG, DAG, dan TAG adalah masing-masing pada 4%, 32%, dan 64%. Bagi mangkin komposit Ni-Zr/AC, penukaran lengkap gliserol dengan kememilihan bagi gelang asetal berahli lima dan enam pada 76% dan 24% masing-masing telah dicapai. Mangkin $Mg_{1.2}Ca_{0.8}O_2$ pula digunakan untuk proses pengesteran gliserol dengan dimetil karbonat dan penukaran gliserol 100% dengan hasil gliserol karbonat hampir 100% telah dicapai. Sebagai kesimpulan, penemuan dalam kajian ini mungkin menyumbang terhadap penggalakan industri biodiesel menerusi pembangunan produk-produk sampingannya.

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ABSTRACT

The escalating growth of biodiesel industry worldwide has led to generate an abundance of glycerol, which affects the biodiesel economy. Thus, this research emphasized on the conversion of glycerol to valuable chemicals "oxygenated fuel additives". Glycerol was separately transformed to diversified components (glycerol acetates, glycerol acetals, and glycerol carbonate) via four different catalytic reaction processes (acetylation with acetic acid, transesterification with methyl acetate, acetalization with acetone, and transesterification with dimethyl carbonate). To achieve these goals, different heterogeneous catalysts were synthesized to facilitate the production of the aforementioned components. As such, sulphated activated carbon, β-MoO_3 functionalized hybrid SBA-15, and Yttrium grafted SBA-3 catalysts were synthesized and accordingly employed for the acetylation of glycerol with acetic acid. The synthesized catalysts were characterized to study their textural properties, nature of their functional groups, and their surface morphology by BET, FTIR, XRD, SAXS, ^{31}P MAS NMR, surface acidity and basicity, CHNS/O, EDX, SEM and TEM. Mono-, di- and triacetyl glycerol (MAG, DAG and TAG, respectively) were the products of acetylation reaction and transesterification reaction with methyl acetate. Five and six membered ring acetals were the acetalization reaction products, and the valuable glycerol carbonate was the product of glycerol transesterification with dimethyl carbonate. To enhance the productivity of DAG and TAG, transesterification reaction of glycerol with methyl acetate was

then investigated over Yttrium grafted SBA-3 catalyst. In context, 3%Y/SBA-3 with its extremely high surface area (1568 m^2 g^{-1}) was the most active catalyst for the acetylation of glycerol achieving complete glycerol conversion with corresponding selectivity of 10%, 35%, and 55% toward MAG, DAG, and TAG, respectively. The same catalyst was highly active during the transesterification of glycerol with methyl acetate leading to complete glycerol conversion with selectivity of 4%, 32%, and 64% toward MAG, DAG, and TAG, respectively, using molar ratio of glycerol/methyl acetate of 1:12 at 110 ^oC. Over Ni-Zr/AC composite catalyst, complete conversion of glycerol with selectivity of 76% and 24 % toward five and six membered ring acetals were obtained via the acetalization reaction. Whereas, $Mg_{1.2}Ca_{0.8}O_2$ catalyst was employed during the transesterification of glycerol with dimethyl carbonate, and 100% glycerol conversion with almost 100% yield of glycerol carbonate were obtained. The stability of the prepared catalysts was also investigated via leaching and reusability tests. Also, the reaction kinetics for the aforesaid reactions was studied and the corresponding kinetics parameters were calculated using POLYMATH 5.1 software. As a result, the findings attained in this study might contribute towards promoting the biodiesel industry through utilization of its by-products.

CHAPTER ONE

INTRODUCTION

1.0 World energy demand for renewable sources

The vast increase of the global energy demands, the forecasted declining of the fossil fuels and the growing environmental concerns to limit the noxious emissions had motivated the search for alternative fuels that are not only cleaner, sustainable and efficient but also inexpensive (Fazal et al., 2011; Manzano-Agugliaro et al., 2013; Milazzo et al., 2013). Hence, the search for sustainable energy from renewable resources like biomass, wind, solar, water and other clean energy sources will contribute to compensate part of the global energy usage in the coming era. Recently, biodiesel has been categorized as "future fuel", being the most attractive substitute to the conventional petro-diesel due to its benign environmental impact (Atabani et al., 2013). It is a non-petroleum based fuel that comprises of fatty acid alkyl esters synthesized through the transesterification and/or esterification reaction of triglycerides (TGs) of fatty acids (C_{12}-C_{22}) with short chain alky source such as methanol, ethanol, propanol or recently dimethyl carbonate (Yaakob et al., 2013; Yunna and Ruhang, 2013).

It is an established fact that biodiesel can be produced via two common synthetic routes; the alkali catalyzed transesterification of TGs or the acid catalyzed esterification of the free fatty acids (FFAs). In the former, glycerol is generated as a by-product, whereas the latter process generates water as a co-product (Alvarez et al., 2010; Ayoub and Abdullah, 2012). The surplus amount of glycerol generated

from the biodiesel industry (10 kg of glycerol for each 100 kg of biodiesel produced) is increasing and thus affecting the biodiesel production process economy (Nair et al., 2012). As such, the predicted increase of biodiesel production will result in the accumulation of glycerol and create a glut in the market. The valorization of this glycerol is a necessity to ameliorate the jeopardized biodiesel economy and to cut down the world biodiesel prices.

Recent research showed that the upgrading of glycerol into valuable commodity chemicals is the novel approach in the research field of glycerol conversion (Rahmat et al., 2010). In particular, the synthesis of valuable oxygenated fuel additives from glycerol represents the hottest topic to investigate. Wide realm of fuel oxygenates could be effectively derived from glycerol (Pagliaro et al., 2009). These include glycerol acetates, glycerol acetals, and glycerol carbonate. Indeed, the syntheses of these components were investigated not only to valorize the biodiesel-derived glycerol, but also to furnish a new generation of fuel additives that are non-toxic, renewable in nature, and more affordable than the conventional fuel additives.

The exhaust emissions from petroleum fuel known to be carcinogenic due to their high content of polycyclic and nitrated polycyclic aromatic hydrocarbons, sulphates, the oxides of carbon and nitrogen, unburned hydrocarbons (UHC), and particulate matter (Gallezot, 2012; Rahmat et al., 2010; Frusteri et al., 2007). It is well known that using traditional fuel additives such as tetraethyl lead (TEL), methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE) and others result in increasing these emissions (Kazuhiko et al., 2005; Suppes et al., 2001). Therefore, it seems imperative to search for new alternative fuel additives replacing those harmful components and this can be truly achieved by formulating new generation of sustainable fuel additives. To be sustainable, it should be derived from renewable

biomass source which has been included in the photosynthesis process. The use of renewable fuel additives can result in cleaner fuel combustion which yields an eco-friendly carbon dioxide to the atmosphere that can contribute to the plants' photosynthesis process and result in a carbon neutral environment.

1.1 Upgrading of glycerol to oxygenated fuel additives

1.1.1 Acetylation of glycerol with acetic acid

Acetylation is the term used to describe a reaction that involves the addition of an acetyl group (C_2H_3O) into a chemical compound. The reaction produces a specific ester, namely the acetate via the replacement of the hydrogen atom of a hydroxyl group with an acetyl group. For instance, the synthesis of glycerol acetates can readily be achieved via the acid catalyzed reaction of glycerol with acetic acid as the acetyl group source (Balaraju et al., 2010). The reaction is reversible and the tendency to attain equilibrium depends on the operational conditions. The forward reaction can be favored by using an excess of acetic acid and the presence of a highly acidic catalyst could accelerate and control the equilibrium to obtain a high acetate yield (Reddy et al., 2012; Gallezot, 2012). In other words, the reaction pathway and the productivity of the desired glycerol acetates will mainly depend on the nature of the catalyst, glycerol to acetic acid molar ratio, reaction temperature and the reaction duration.

Traditionally, glycerol acetylation is performed using different homogeneous catalysts, which offered high yield of products and mild operating conditions (Zhou et al., 2008; Pagliaro et al., 2009). However, the use of conventional homogeneous acid catalysts must be limited in the future to comply with the strict environmental regulations (Alvarez et al., 2010). The use of these catalysts have shown some

demerits which have made the cost of fuel additives produced by using them highly expensive (Rao et al., 2006). Some of these demerits include complete product removal and catalyst separation. Contrary to the heterogeneous, homogeneous catalysts cannot be recycled and their direct disposal is highly restricted. Thus, one of the objectives this work has addressed is the development of suitable heterogeneous catalysts that are reliably efficient, reusable and thereby can make the cost of fuel additives more affordable. This is because with heterogeneous catalyst, product separation is easier and reusability of the catalyst is possible. Catalyst properties such as surface area, pore size, pore volume, particle size, thermal stability and structure have been properly investigated during catalyst preparation to achieve the best reaction conversion and higher yield of the desired products.

1.1.2 Transesterification of glycerol with methyl acetate

The process of transforming an ester into another via the interchanging of the alkoxy moiety is called transesterification (Kin et al., 2007). In general, the reaction is catalyzed by acid catalysts which donate a proton to the carbonyl group and make it more potent electrophile. The reaction offers an alternative pathway for the synthesis of the valuable glycerol acetates, which were previously produced by glycerol acetylation with acetic acid. Morales and coworkers have recently reported this reaction as the first approach (Morales et al., 2011). They obtained complete conversion of glycerol by using a high molar ratio of glycerol to methyl acetate (1:50) and a high loading of sulfated SBA-15 catalyst (7.5 wt.% with respect to glycerol) at 170 ^{o}C.

1.1.3 Acetalization of glycerol with acetone

The acetalization or acetalisation reaction is the process mostly used in organic synthesis to protect the carbonyl group of ketones and aldehydes. In this reaction, acetals are produced by the reaction of aldehydes (or ketones) with alcohols in the presence of an acid catalyst (Wiles et al., 2005). The acetalization of glycerol with aldehydes and/or ketones was intensely studied by many researchers (Deutsch et al., 2007; Silva et al., 2010; Reddy et al., 2011). The reaction of glycerol with aldehydes was performed at relatively high temperature (Agirre et al., 2011) and in the presence of organic solvents (Monbaliu et al., 2011). The acetalization reaction with aldehydes generates five and six membered ring acetals. Whereas lower reaction temperature was required for the reaction of glycerol with ketones, the process furnishes mainly the five membered ring acetal.

1.1.4 Transesterification of glycerol with dimethyl carbonate

Various synthetic routes for the production of the valuable glycerol carbonate were reported in the literature such as the direct carboxylation of glycerol with CO_2 (Aresta et al., 2006; Ochoa-Gómez et al., 2011) and the reaction of glycerol with urea (Hammond et al., 2011). Recently, the transesterification of glycerol with alkyl carbonates was introduced as an environmental pathway for the synthesis of glycerol carbonate. In context, the activity of different alkali homogeneous and heterogeneous catalysts was tested for this reaction. According to the reported studies, there exists an unfilled research gap in the development of highly stable and more efficient heterogeneous catalyst for this reaction and also reducing the reaction conditions to bring down the production cost of glycerol carbonate.

1.2 Problem statement

It is certain that a good society needs a good health condition and to achieve this, our environment, in totality must be protected from any kind of threats. It is also a known fact that the hazardous emissions from petroleum fuel are in part major cause of environmental pollution (Ribeiro et al., 2007). In this era, the expansion of transportation system in most urban centers, the soaring of world population, the increasing prices of the petroleum fuel and the increasing campaign for clean combustion systems have necessitated the search for alternative solutions (Atabani et al., 2013). Many countries have embarked on the use of biodiesel or biodiesel/petro-diesel blends as successful alternatives to reduce the dependence on crude petroleum (Bagley et al., 1998). Currently, the worldwide production of biodiesel is increasing exponentially and thus resulting in generating colossal amounts of glycerol (Balaraju et al., 2010). The co-production of crude glycerol will affect the economy of the biodiesel industry and result in superfluity in the world glycerol market. Thus, finding new destinations for this glycerol is a necessity to improve the overall economy of the biodiesel industry. On the other hand, the modern automobile industry depends mainly on economizing the air/fuel (A/F) ratio and the high power production by improving the engine's fuel quality (Bhale et al., 2009). To achieve this goal, different exhaustible fuel additives are being added to the engine fuel as octane number (ON) boosters, nozzle flow improvers, anti-freezing agents, and viscosity enhancers (Frusteri et al., 2007). The combustion of those fuel blends in automobile engines generates huge amounts of carcinogenic substances such as CO, CO_2, NO_x, UHC, and a variety of particulate matter (Frusteri et al., 2007). Recently, the use of some fuel additives such as TEL, MTBE, ETBE, and others has been prohibited due to their malign environmental impacts (Frusteri et al., 2007).

Therefore, the search for sustainable alternative additives derived from glycerol is the hottest issue in this research area. Today, there is an increasing number of vehicles in Malaysia leading to a substantial increase of hazardous emissions from their engines and thereby makes the environment unsafe.

One of the possible solutions which depend on the availability of feedstock and the current research for the utilization of biodiesel-derived glycerol to produce eco-friendly components is the selective heterogeneous catalysis. For instance, the yield of valuable diversified components like di- and triacetyl glycerol (DAG and TAG), glycerol acetals (five and six membered ring acetals), and glycerol carbonate can be enhanced by proper choice of effective heterogeneous catalysts. The use of solid (heterogeneous) catalysts offers variety of merits such as the ease of separating them from the reaction products, being reusable, high selectivity of the favored products, and further application in continuous packed bed reactors. However, one of the demerits accompanying the use of heterogeneous catalysts is the presence of multi-phases reaction system (Vapor-Liquid-Solid) and thus, relatively high reaction temperature and pressure are required to ensure best contact of the reaction components.

According to the literature, none of the reported studies about the acetylation of glycerol with acetic acid achieved TAG yield higher than 50% using a low molar ratio of reactants and at a temperature lower than 120 ^{o}C (Gonçalves et al., 2008; Balaraju et al., 2010). Moreover, most of the previously used heterogeneous catalysts were either costly or non-reusable and in some cases complex to prepare (Gonçalves et al., 2008; Ferreira et al., 2009a). Therefore, this research seeks to investigate the synthesis of suitable heterogeneous catalyst that can effectively bring down the operational conditions and thereby the cost of the produced oxygenated fuel additive

(DAG and TAG).

In the case of glycerol transesterification with methyl acetate, it has been found that only one research paper reported on this reaction. In that work, glycerol was completely converted by using a high molar ratio of glycerol to methyl acetate (1:50) and a high loading of sulfated SBA-15 catalyst (7.5 wt.% with respect to glycerol) at high temperature of 170 ^{o}C (Morales et al., 2011). Therefore, the present research aims at developing a high surface area silica-based catalyst that can be employed to increase the yield of DAG and TAG and to bring down the cost of the process. It is therefore believed that this work will represent the breakthrough for the synthesis of TAG from glycerol.

In the case of glycerol acetalization, the present work seeks to synthesize highly efficient Ni-Zr composite catalyst that can facilitate the synthesis of both acetals (five and six membered) via the reaction of glycerol with acetone at mild reaction conditions. It is worth of note that none of the reported studies emphasized on the synthesis of both acetals (five and six ring components) from acetone.

The synthesis of glycerol carbonate via the transesterification of glycerol with dimethyl carbonate was reported over variety of homogeneous and heterogeneous catalysts. None of the reported works emphasized on using low cost, easily prepared, reusable and highly active heterogeneous catalyst. In addition, complete conversion of glycerol with 100% yield of glycerol carbonate was not reported in the literature. Therefore, the present work aims to develop mixed oxide (Ca-Mg) heterogeneous catalyst to achieve the aforementioned goals such as high effectiveness, selective performance, stability of activity, and simplicity of preparation methods.

1.3 Research objectives

The present research work is aimed at developing highly efficient heterogeneous catalysts to synthesize diversified oxygenated fuel additives (glycerol acetates, glycerol acetals and glycerol carbonate) from glycerol via acetylation with acetic acid, transesterification with methyl acetate, acetalization with acetone, and transesterification with dimethyl carbonate. The specific objectives are:

i. To develop an effective silica-based heterogeneous catalysts for the synthesis of DAG and TAG from glycerol via acetylation and transesterification reactions.

ii. To develop activated carbon-based Ni-Zr metal composite heterogeneous catalyst for the synthesis of five and six membered glycerol acetals from glycerol via acetalization with acetone.

iii. To develop heterogeneous mixed metal oxides (Mg and Ca) catalyst for the transesterification of glycerol with dimethyl carbonate to synthesize the valuable glycerol carbonate.

iv. To characterize the developed catalysts for their morphology, crystalline structure, textural and surface functional properties.

v. To investigate the catalytic performance and the reusability of the developed catalysts and the variation in process parameters (molar ratio of reactants, catalyst amount, reaction temperature and time) during all the studied glycerol reactions.

vi. To study the reaction kinetics of glycerol acetylation with acetic acid, transesterification with methyl acetate, acetalization with acetone, and transesterification with dimethyl carbonate.

1.4 Scope of study

The scope of the present study covers the development, characterization, and activity tests of different heterogeneous catalysts (sulfated AC catalyst, β-MoO3 functionalized hybrid SBA-15 catalyst, yttrium grafted SBA-3 catalyst, Ni-Zr/AC catalyst, and $Mg_{1.2}Ca_{0.8}O_2$ catalyst) for glycerol acetylation with acetic acid, transesterification with methyl acetate, acetalization with acetone, and transesterification with dimethyl carbonate. It also involves the characterization of the developed catalysts, and the evaluation of the effects of operational parameters in the stated reactions.

The main goal of this research is to develop reusable, highly active and eco-friendly heterogeneous catalysts for the synthesis of different fuel additives from glycerol. The plan of this research is to investigate the synthesis of glycerol acetates (DAG and TAG) using an economic molar ratio of glycerol to acetic acid (<1:6) at relatively low temperature (<120 ^{o}C). The present work also aims to carry out the transesterification of glycerol with methyl acetate using a molar ratio of glycerol to methyl acetate less than 1:50 and at reaction temperature lower than 170 ^{o}C. In another approach, the current work investigates the synthesis of five and six membered glycerol acetals via the acetalization of glycerol with acetone at mild conditions (reaction temperature below than 75 ^{o}C and reaction time less than 4 h). The synthesis of glycerol carbonate would be investigated using a molar ratio of glycerol to dimethyl carbonate less than 1:3 and at reaction temperature lower than 75 ^{o}C.

This is an attempt to ameliorate the economy of the biodiesel industry and promote the production of the sustainable fuel additives. It is hoped that the herein developed catalysts can help to lower the cost of fuel additives production and

overcome some (if not all) of the drawbacks associated with the homogeneous processes.

1.5 Organization of the thesis

This thesis consists of five chapters; each of them represents an integral part of the main work that is sequentially arranged. The content of each chapter is given in brief as follows.

Chapter one (Introduction)

This chapter presents an overview of the environmental problems associated with the use of petroleum fuel and the impact of using exhaustible fuel additives. It also enumerates and points out the reactions of glycerol to be studied in this work. The problem statement, research objectives, scope of work, and organization of the thesis are also covered in this chapter.

Chapter two (Literature review)

This chapter discloses review on the proposed reactions in the area of the present study. It also divulges a depicture on the challenges and benefits ahead (future work) as it presents the unfilled research gaps in each of the herein studied reactions. It reviews the conducted studies prior to this work in terms of the reaction conditions and the achieved results in order to figure out the shortcomings, and areas of need for improvement.

Chapter three (Materials and methods)

This chapter succinctly lists the materials, chemicals, and the equipment used in this work. The research methodology employed in this study is well presented

here. Detailed experimental setup including the preparation of each of the heterogeneous catalysts, description of the reaction procedures, and the characterization of the prepared catalysts are outlined in this chapter.

Chapter four (Results and discussion)

This chapter is the main thrust of this thesis as it presents the outcome of the present investigation, interprets and analyzes the obtained results. In order to provide ideal flow of the information, the chapter is divided into four major sections; the acetylation of glycerol with acetic acid, transesterification of glycerol with methyl acetate, acetalization of glycerol with acetone, and transesterification of glycerol with dimethyl carbonate. In each section, the characterization and the activity test of each of the prepared catalysts were presented and accordingly, a brief discussion was laid. The effects of different operational parameters are explained as the case may be. Lastly, the chapter includes the results and discussion of the kinetic studies made for each reaction.

Chapter five (Conclusions and recommendations)

This chapter presents brief conclusions of the findings of this research and the suggested recommendations for future studies in the field of synthesis of heterogeneous catalysts and improvements required in fuel additives production.

CHAPTER TWO

LITERATURE REVIEW

2.0 Introduction

This chapter presents a review of the previous investigations on the catalytic upgrading of glycerol to fuel additives. It provides an overview on glycerol and its synthesis routes; explains the significance of using fuel oxygenates; analyzes the reported studies in terms of the reaction conditions applied, details the role of various catalysts in the acetylation, acetalization, and transesterification processes, and justifies the decision for choosing various materials as heterogeneous catalysts in the current studies. It also highlights the influence of different operational parameters on the aforementioned reactions.

2.1 Glycerol

Glycerol is a chemical compound with the formula $HOCH_2CH(OH)CH_2OH$ which has an IUPAC name of 1,2,3-propanetriol. Its chemical discovery was first in 1779 by the Swedish chemist Karl Wilhelm Scheele, during the saponification of olive oil. Since the late 1940ies, synthetic glycerol was mainly manufactured from the hydrolysis of epichlorohydrin– a product from the chlorination of allyl alcohol (Figure 2.1). Interestingly, this process is currently reversed and epichlorohydrin can

now be produced from glycerol due to the abundance of this feedstock (Zhou et al., 2008). In addition, glycerol can also be obtained as a main product from the fermentation of sugars like glucose and fructose (Cheng et al., 2000) or as a co-product of the ethanol production process from lignocellulose (Rogers et al., 2005). The most important physical and chemical properties of glycerol are viewed in Appendix A.

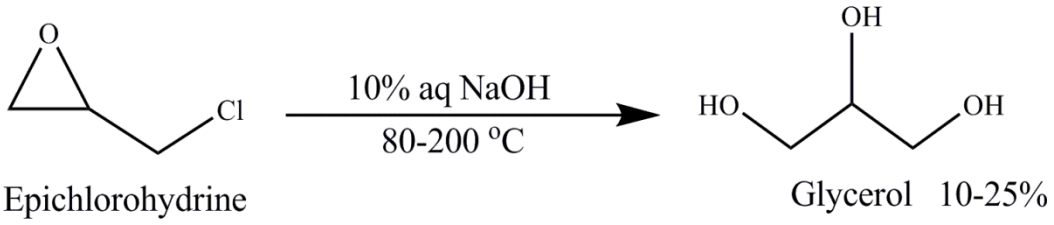

Figure 2.1. Synthesis of glycerol from Epichlorohydrin.

Commercially, glycerol has been classified into two grades; biocompatible and industrial according to its purity and synthetic route. Industrial grade glycerol is usually obtained as a by-product from different processes. The gross co-production of glycerol is increasing considerably on industrial scale, either from saponification reaction of fats and oils with sodium hydroxide to yield soaps and glycerol (Fangxia et al., 2012) (Figure 2.2, X= ONa), catalytic hydrolysis of fats/ oils to produce fatty acids and glycerol (Zhou et al., 2008) (Figure 2.2, X= OH) or from transesterification of vegetable oils with alcohol (methanol, ethanol) to yield fatty acids (methyl, ethyl) esters (FAME, FAEE, respectively) and glycerol (Figure 2.2, X= OCH_3).

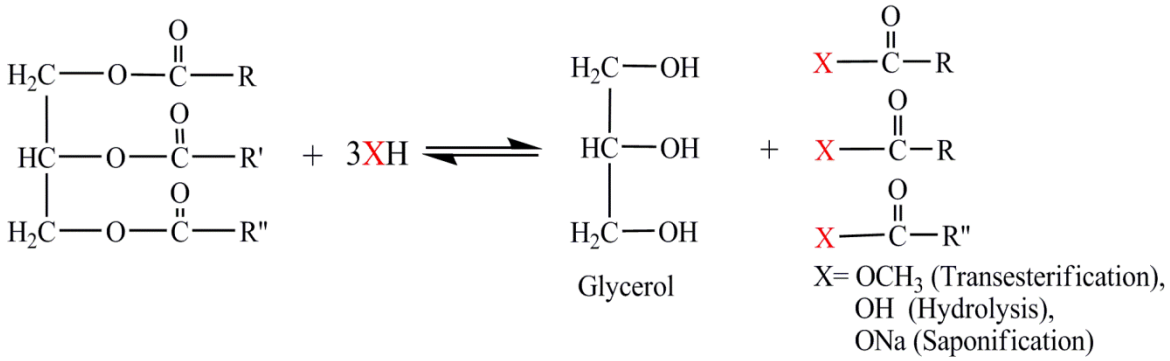

Figure 2.2. Glycerol by-production by various chemical routes (Zhou et al., 2008).

2.2 Glycerol from biodiesel industry

The immense increase of the world energy demands, the foreseen depletion of the fossil energy sources and the growing environmental concerns to limit exhaust emissions had motivated the quest for alternative fuels that are not only cleaner, sustainable and efficient but also more affordable (Bagley et al., 1998; Zhou et al., 2008). Recently, biodiesel has been categorized as a "green fuel", being the most attractive substitute to the conventional petro-diesel. It is a non-petroleum based fuel that compose of fatty acids alkyl esters synthesized through the transesterification and/or esterification reaction of triglycerides (TGs) of fatty acids (C_{12}-C_{22}) with short chain alky source (methanol, ethanol, propanol or recently dimethyl carbonate) (Gerpen, 2005). The reaction generates glycerol as the main by-product with about 100 kg of crude glycerol for each ton of biodiesel produced (Figure 2.3). This will create a superfluity in the world glycerol market and thereby will ruin growing biodiesel industry (Gupta and Kumar, 2012).

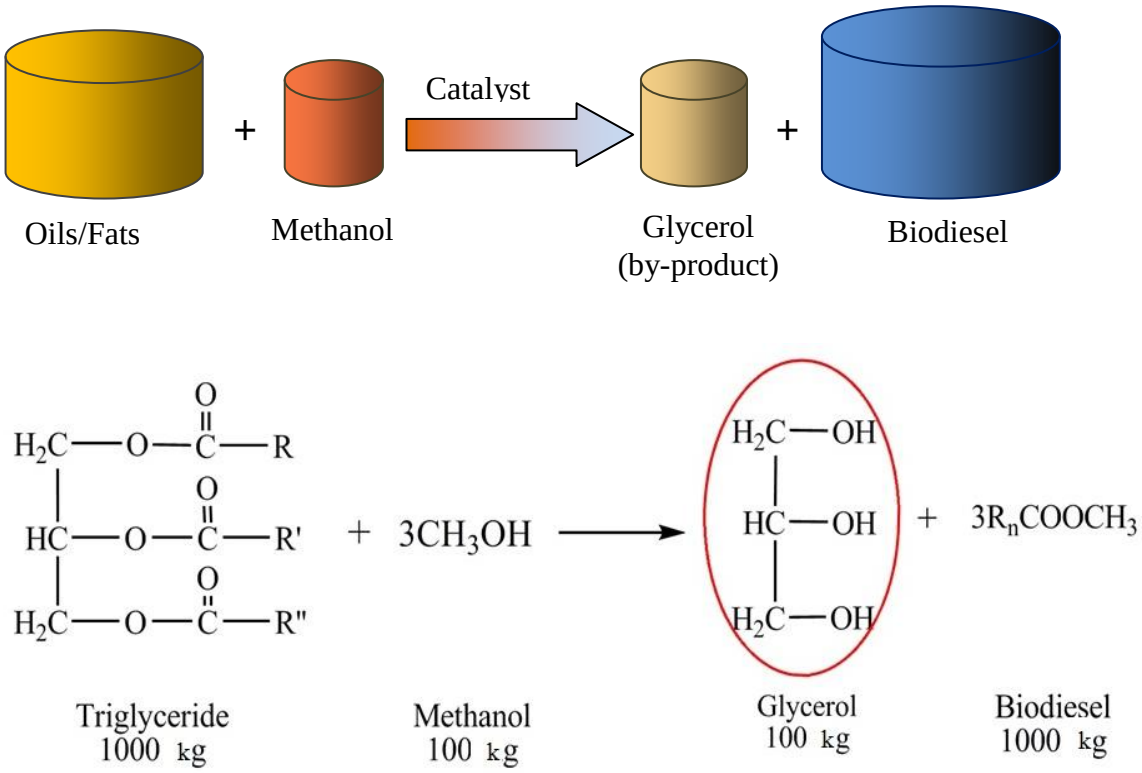

Figure 2.3. Synthesis of biodiesel via the transesterification of oils/fats with methanol, adapted from (Balaraju et al., 2010).

The by-produced glycerol contains a mixture of methanol, catalyst residue, unreacted mono-, di- and triglycerides, water, methyl esters, free fatty acids, and other organic materials, depending on the biodiesel process (Zhou et al., 2008). Thence, there are limited direct uses of this glycerol (with an approximate 50% purity) and also low economic valued. Another environmental aspect related to its disposal as the methanol content of glycerol categorizes it as hazardous waste. Although further treatments of crude glycerol are applied (Figure 2.4), the utilization of the biodiesel-derived glycerol for biocompatible purposes is still infeasible. The treatments encompass neutralization with phosphoric acid using potassium hydroxide catalyst, so that the formed potassium phosphate salt can be used as fertilizer. A vacuum flash process is usually used to remove the methanol in the

crude glycerol. The addition of citric acid solution during the treatment process is to inactivate the remaining traces of the catalyst and to eliminate the catalytic effects. This process furnishes glycerol with an estimated purity of 85-95% depending on the separation process efficiency (Bournay et al., 2005). The as-obtained glycerol is typically categorized as industrial grade and sold at low prices (Tyson et al., 2004). Further refining using vacuum distillation or ion exchange processes can take the purity of glycerol up to 99.7% (Gerpen, 2005; Zhou et al., 2008). However, it seems infeasible for small biodiesel plants to refine the crude glycerol with such processes and therefore they discard it as waste.

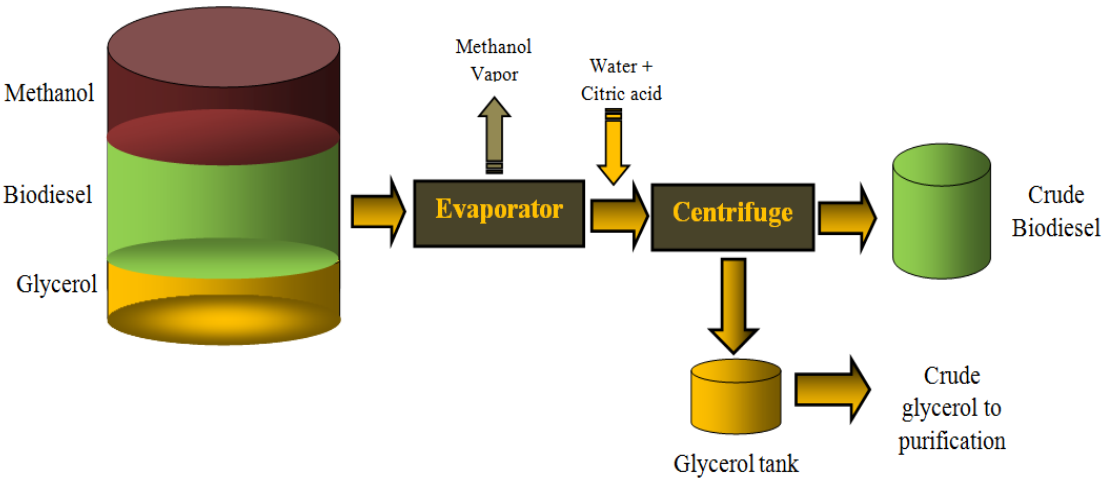

Figure 2.4. Separation of crude glycerol from biodiesel (Bournay et al., 2005).

During the last decade, the worldwide biodiesel production has increased dramatically due to its environmental impacts and the fact that it is renewable in nature (Bhale et al., 2009). This is the logical reason for the exponential increase of glycerol quantities in the market. Nowadays, the European glycerol market is flooded with the impure glycerol coming from biodiesel industry. It is forecasted that the world glycerol prices to be affected by biodiesel production by an inverse linear

relationship between the cost of biodiesel production and glycerol prices variation in the market, with an increase of US$2.2/ton for each US$22 reduction in glycerol price per ton (Haas et al., 2006). Therefore, there is an imperative necessity to find more economical destinations for this glycerol. It will be beneficial to the research community and biodiesel industry in understanding the utilization of this aggravating glycerol to high-value chemicals (fuel additives) and for reference in their plans for sustainable and profitable biodiesel production. In this context, many research projects and studies have been geared toward the transformation of the low value glycerol via different techniques and approaches (Zhou et al., 2008; Gupta and Kumar, 2012). The innovative development of glycerol-based fuel additives could assist to ameliorate the biodiesel industry and contribute toward replacing the controversial tertiary alkyl ethers (MTBE and ETBE).

2.3 Glycerol transformation into value-added chemicals

Glycerol is an abundant carbon-neutral renewable feedstock for the synthesis of different biomaterials as well as source for a variety of valuable commodity chemicals (Pagliaro et al., 2009; Rahmat et al., 2010; Gallezot, 2012). Due to its three hydroxyl groups attached to the bone carbon atoms, glycerol molecule can either be converted to different intermediate or final chemical products or be fragmented to smaller valuable outlets. According to Table 2.1, wide realm of chemical products with variety of applications can be derived from glycerol. Recently, many research projects have been devoted to the conversion of this renewable polyol by various catalytic processes such as oxidation process to obtain dihydroxy acetone, glyceraldehyde, glyceric acid, glycolic acid and hydroxyl pyruvic acid (Augugliaro et al., 2010; Liebminger et al., 2009), fermentation process to

obtain 1,3-propanediol and 2,3-butanediol (Metsoviti et al.), acetylation or esterification process with acetic acid toward glycerol esters (Rahmat et al., 2010; Fangxia et al.**,** 2012), transesterification process with alkyl carbonates to synthesize the valuable glycerol carbonate (Li and Wang, 2010; Simanjuntak et al., 2011), etherification process with or without solvents to obtain glycerol ethers (Polyglycerols) (Ayoub et al., 2012; Gupta and Kumar, 2012; Lee et al., 2010; Xiao et al., 2011), and acetalization with aldehydes or ketones to obtain five and six membered ring acetals and ketals (Reddy et al., 2011; Serafim et al., 2011).

Table 2.1. List of currently available glycerol outlets with their applications.

product	Reaction	Usage	Field of application	Reference
Succinic acids	Glycerol fermentation by *Anaerobiospirillum succiniciproducens*	Building block for the synthetic resins and biodegradable polymers	Resins and plastic industry	(Lee et al., 2001)
Dihydroxy acetone	Glycerol oxidation	Tanning and moisturizing agent	Cosmetics	(Demirel-Gülen et al., 2005; Gil et al., 2011)
Docosahexaenoic acid (DHA)	Crude glycerol with microalgal culture	Important omega-3 polyunsaturated fatty acid (v-3PUFA) with medically established therapeutic capabilities Against cardio vascular diseases, cancers, schizophrenia, and Alzheimers, also an essential nutrient during early Human development	Pharmaceutical, Nutrient	(Chi et al., 2007)
Propylene glycol (1,2-propanediol)	Glycerol hydrogenolysis	Polyester resins, liquid detergents, pharmaceuticals, cosmetics, tobacco humectants, flavors and fragrances, personal care, paints, animal feed, antifreeze, etc.	Antifreeze and de-icing agents replacing the toxic ethylene glycol-based products	(Pagliaro et al., 2009; Rahmat et al., 2010; Zhou et al., 2008)
Hydrogen	Glycerol reforming	Electrical power generation, Hydrogen fuel cells	Fuel, Power	(Pagliaro et al., 2009; Rahmat et al., 2010)
2,3-Butanediol	Glycerol fermentation by *Klebsiella oxytoca*	Intermediate for the synthesis of Methyl-Ethyl-Ketone (MEK)	Effective fuel additive	(Metsoviti et al., 2012; Cheng et al., 2010)

Table 2.1. continued.

product	Reaction	Usage	Field of application	Reference
Acrolein	Glycerol dehydration	Staring chemical for the synthesis of Acrylic acid, acrylic acid esters, and detergents	Chemicals synthesis	(Rahmat et al., 2010)
Glycerol acetates or esters	Glycerol acetylation or esterification	Cetane improvers, Anti-knocking agents, Octane boosters, flow properties improvers,	Fuel additives	(Balaraju et al., 2010; Reddy et al., 2010)
Glycerol ethers	Glycerol etherification	Octane improvers, cold flow improvers and viscosity reducers for biodiesel	Fuel additives, Ployemrs	(Gupta and Kumar, 2012; Lee et al., 2010; Xiao et al., 2011; Rahmat et al., 2010)
Glycerol carbonate	Glycerol transesterification	Protic solvent (in resins and plastics), chemical intermediate, fuel stabilizer additive, wetting agent for cosmetics and carrier solvent for medical preparations valuable intermediate for the synthesis of: glycidol, poly urethane protecting coatings for wood and metal substrates	Fuel additive and chemicals synthesis	(Climent et al., 2010; Ochoa-Gómez et al., 2011)
Glycerol acetals	Glycerol acetalization	Anti-freezing agents for biodiesel	Fuel additives	(Reddy et al., 2011; Serafim et al., 2011)

Table 2.1. continued.

product	Reaction	Usage	Field of application	Reference
1,3-Propanediol,	Glycerol fermentation by *Klebsiella oxytoca* or by *Klebsiella pneumoniae*	As starting monomers for the synthesis of Poly trimethylene terephthalate (PTT) and Polyethylene terephthalate (PET)	Plastic, textile and fiber industries	(Metsoviti et al., 2012; Huang et al., 2012)
Ethanol	Glycerol fermentation by *Klebsiella oxytoca* or by *E-coli*	Mostly used as fuel and fuel additive, also a fuel for bipropellant rocket Fuel cells, Chemical intermediate for the synthesis of several organic compounds like ethyl halides, ethyl ester, acetic acid, butadiene, ethyl amines, Used as anti septic and antidote for poisonous and toxic chemicals for medical purposes	Fuel cells, Medical, Chemicals synthesis	(Rahmat et al., 2010; Gupta and Kumar, 2012)

Glycerol transformation into fuel oxygenates by means of acetylation, acetalization, and transesterification and by etherification reactions are of high interest to the research community since they assist to ameliorate the jeopardized economy of biodiesel industry by utilizing its by-product and contribute toward improving the biodiesel properties (Bhale et al., 2009; Smith et al., 2010; Gallezot, 2012). Glycerol acetals (Reddy et al., 2011; Serafim et al., 2011), glycerol ethers (Ayoub et al., 2012; Lee et al., 2010; Pagliaro et al., 2009), acetyl glycerol (Rahmat et al., 2010; Reddy et al., 2010), and recently glycerol carbonate (Climent et al., 2010; Ochoa-Gómez et al., 2011; Simanjuntak et al., 2011; Zhou et al., 2008) have found enormous potential applications as fuel/biodiesel additives replacing those of depleted sources (Pagliaro et al., 2009; Rahmat et al., 2010; Serafim et al., 2011). These derivates are of great importance as fuel additives when added to fuel/biodiesel formulation due to their prominent impact in decreasing the noxious emissions in the exhaust gas, and in particular, carbon monoxide (CO), unburned hydrocarbons (UHC) and particulate matter (PM) emissions (Zhou et al., 2008). In addition, they act as viscosity reducers (Pagliaro et al., 2009), anti-freeze agents (Silva et al., 2010b), cold flow improvers for biodiesel (Rahmat et al., 2010) and as antiknock additives for gasoline (Melero et al., 2007b; Delfort et al., 2005). Moreover, these glycerol outlets can also be applied as octane boosters for gasoline, as an alternative to the traditional tertiary alkyl ethers (MTBE and ETBE) (Bradin et al., 2007; Fangxia et al., 2012). In context, limited number of studies dealing with the catalytic upgrading (acetylation, acetalization and transesterification) of glycerol to fuel additives were recently reported, mainly using supported heterogeneous catalysts (Figure 2.1). This explains the great potential of using glycerol for the synthesis of

promising commodity chemicals and open new approaches for the research community and industry to develop both the catalytic materials and technologies needed for the efficient conversion of glycerol into variety of desired products.

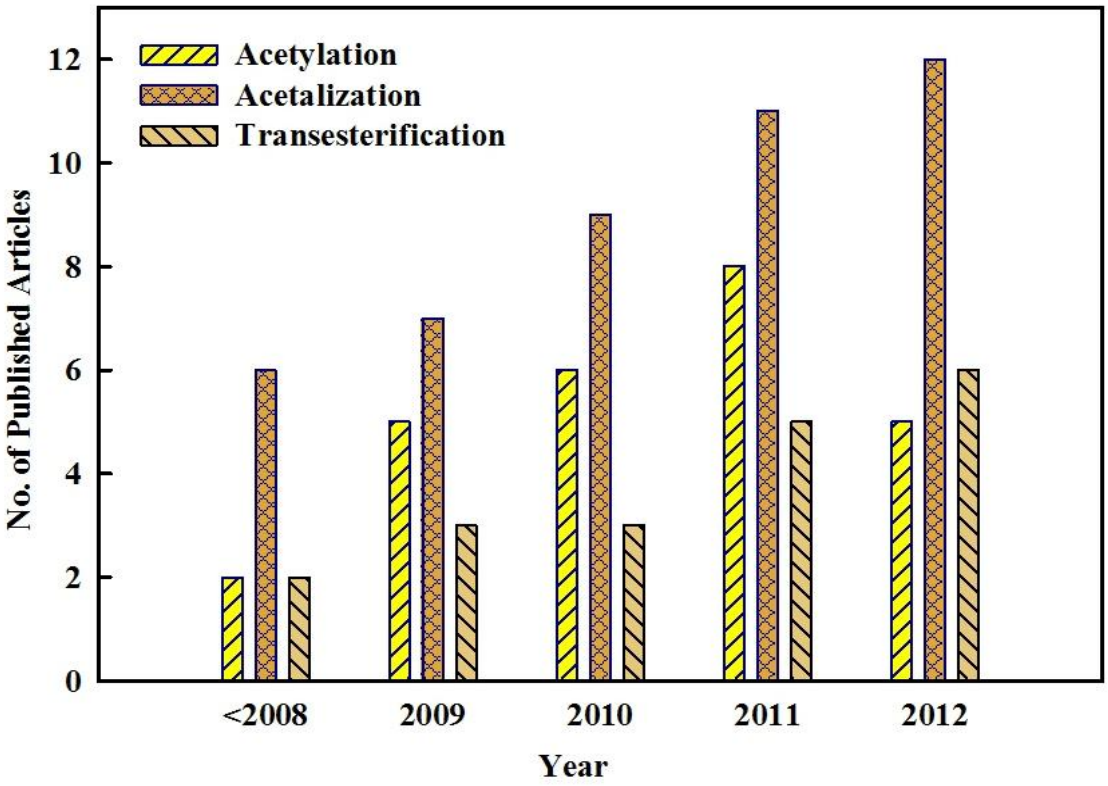

Figure 2.5. The number of published research articles, obtained from Google search engine using keywords of glycerol, glycerol acetylation, glycerol esterification, glycerol acetates, glycerol esters, glycerol acetalization, glycerol acetalisation, glycerol acetals, glycerol transesterification, glycerol carbonate, glycerol carbonation, dimethyl carbonate, methyl acetate, monoacetin, diacetin, triacetin, bioadditives, fuel oxygenates, and biodiesel additives). Access date on 02.July.2012 at 02:30 pm.